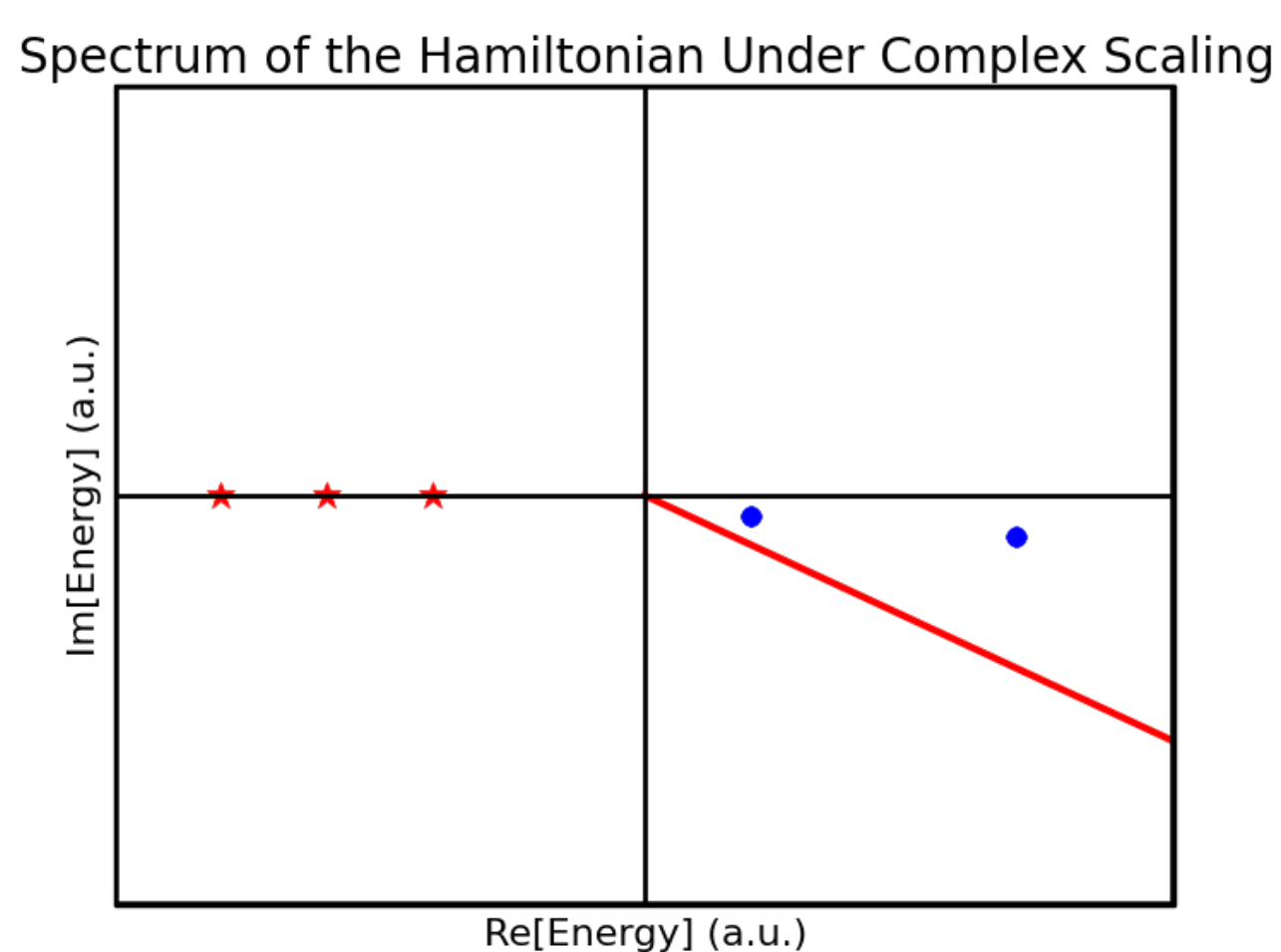


Introduction

Metastable electronic states of molecules pose an interesting problem to theorists. The difficulty comes from the fact that such states are not bound and must therefore be treated with the numerically challenging language of scattering theory. However, these states are increasingly important due to the use of high energy radiation for probing molecular processes as well as the discovery of their role in important molecular processes including radiation damage to DNA[1][2]. We present an extension of electronic structure theory to treat these states, also called resonances, in a computationally feasible manner.

Complex scaling

Our approach is based on the theorems of Balslev and Combes[3], and Simon[4]. These theorems establish several important points about the spectrum of a particular class of Hamiltonian operators when the coordinates of the particles are scaled by a complex number:



- the bound energies are unchanged
- the continuum energies are rotated into the lower half plain
- the resonances appear as discrete eigenvalues corresponding to square integrable eigenfunctions
- the real part of the resonance energy is its position
- the imaginary part is the negative half-width.

This allows for the determination of the resonance energies $E_{\text{res}} = E_r - i\Gamma/2$ using a square integrable basis.

Complex basis functions

In the molecular problem, complex scaling of the electronic coordinates is problematic. This is because the nuclear attraction terms, $|\mathbf{r} - \mathbf{R}|^{-1}$, are not analytic under complex scaling. Note that a matrix element of the complex scaled hamiltonian is equivalent to a matrix element of the bare hamiltonian with complex basis functions:

$$\langle \psi_i(\mathbf{r}) | H(\mathbf{r}e^{i\theta}) | \psi_j(\mathbf{r}) \rangle = \langle \psi_i(\mathbf{r}e^{-i\theta}) | H(\mathbf{r}) | \psi_j(\mathbf{r}e^{-i\theta}) \rangle.$$

If we use a gaussian basis, we can approximate these non-analytic complex basis functions using complex exponents:

$$\exp[-\alpha(\mathbf{r}e^{-i\theta} - \mathbf{A})^2] \approx \exp[-\alpha e^{-2i\theta}(\mathbf{r} - \mathbf{A})^2].$$

The static exchange approximation

In the static exchange approximation, the procedure for determining resonance energies is straightforward. The static exchange hamiltonian for a spin-restricted target is given by

$$H = T + V_{\text{nuc}} + 2J - K.$$

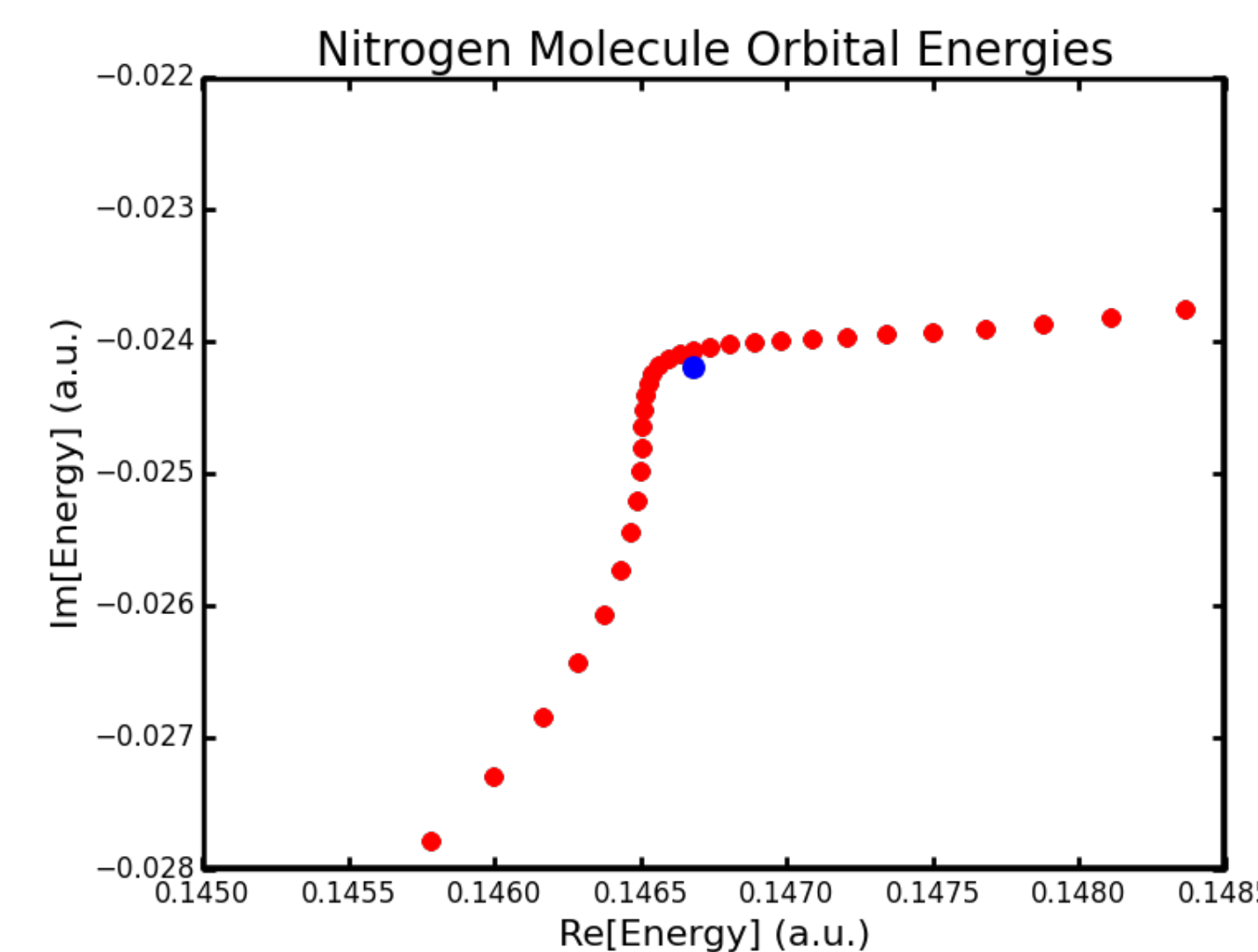
The procedure for determining resonance energies is:

1. determine the electron density of the closed shell target in a real basis
2. diagonalize H in a basis including complex basis functions of the form

$$(x - A_x)^l (y - A_y)^m (z - A_z)^n \exp[-\alpha e^{-2i\theta}(\mathbf{r} - \mathbf{A})^2].$$

3. repeat for many values of θ and look for stabilization.

These stable points are the best approximation to the resonance energy in accordance with a variational principle. An rational analytic continuation of the energy as a function of θ is used to determine this point precisely.



Complex basis sets

In designing complex basis sets, we seek standard basis sets that can be used to converge complex basis function calculations with respect to basis set size. We came up with the following features important to the performance of a complex basis:

- a good description of the valence space
- complex functions on multiple centers
- very diffuse complex functions
- even tempered spacing of less than 2.5 for accuracy of 0.02 eV.

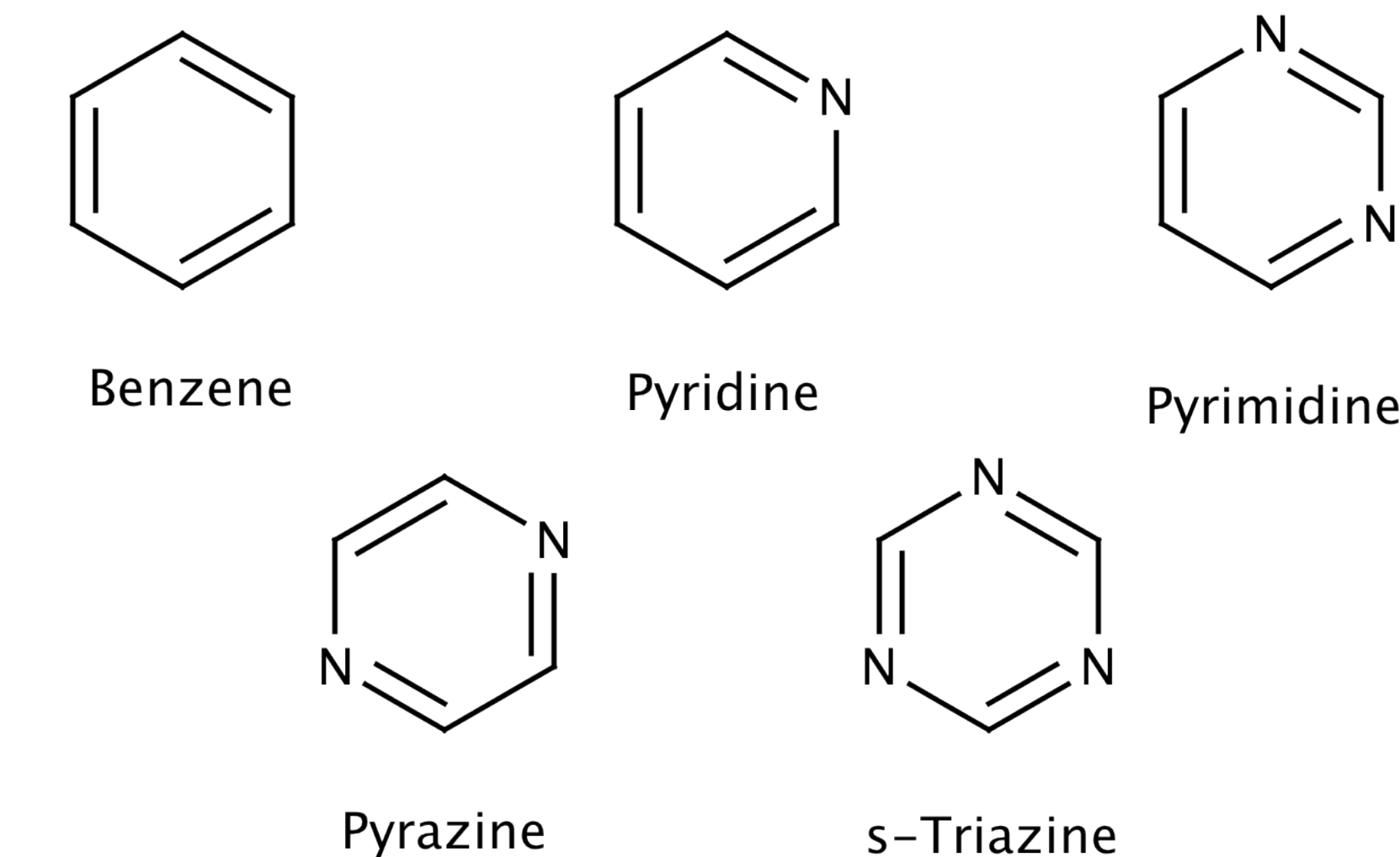
Our solution is to use cc-pvXZ basis sets for the real calculation and then augment them with complex augmented functions and an even tempered set of 7 diffuse functions with an even tempered spacing of 2.3. For main second row elements, we used spd diffuse functions for dz bases, spdf for tz, and so on. We will refer to these basis sets as caug-ccpvXZ bases. The convergence properties of these basis sets appear to be sufficient for small molecules. The results below are all in eV.

Basis	Nitrogen		Formaldehyde		Carbon dioxide	
	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
caug-ccpvDZ	3.98980	-0.65830	2.64813	-0.75697	5.80248	-0.00071
caug-ccpvTZ	3.87613	-0.61104	2.64539	-0.80621	5.53680	-0.37414
caug-ccpvQZ	3.85113	-0.61782	2.60813	-0.79131	5.47779	-0.34736

Application to nitrogen containing aromatic rings

We investigated the metastable states of some nitrogen containing aromatic compounds. These compounds are interesting because there is some disagreement over the sign of their electron affinities. Nenner and Schulz [5] report that pyrazine, pyrimidine, and s-triazine all have bound anions, while others have found otherwise [6][7]. CCSD(T) calculations of adiabatic and vertical electron affinities show no bound anions in any of these molecules.

We will use the convention that negative electron affinities correspond to bound anions. Electron affinities are expressed in kilocalories per mole. The calculations were done in the aug-ccpVTZ basis.



	Benzene	Pyridine	Pyrimidine	Pyrazine	s-Triazine
vertical		23.959	15.602	9.194	10.804
adiabatic	18.167	19.016	9.646	3.269	4.647

Since these electron affinities are all positive, the states are unbound, and we can use the method of complex basis functions to investigate their positions and lifetimes. We used the caug-ccpvDZ basis set. In some cases, the analytic continuation procedure revealed multiple stabilization points corresponding to the same resonance. In these cases, the point that occurs at a smaller scaling angle is taken to be the actual value. The results are shown in eV, and the differences between molecules agree with experiment to within 0.2 eV.

Benzene		Pyridine		Pyrimidine		Pyrazine		s-Triazine	
Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]	Re[E]	Im[E]
3.1288	-0.2646	2.6459	-0.1897	2.3480	-0.1303	2.0809	-0.1590	2.2580	-0.0803
		3.0219	-0.2291	2.7481	-0.1706	2.8258	-0.1660		
9.4297	-1.2191	9.1366	-1.1151	8.8765	-0.9884	8.8740	-1.2838	8.6586	-0.9917

Future work

There is great opportunity for extending these ideas including:

- optimized basis sets
- complex self-consistent-field calculations for resonances
- correlated methods using complex basis functions
- resonance properties and nuclear motion on a metastable potential surface

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